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Detailed Determination of the Metallic Phase Saturation Boundary in the Fe-Ni-Cu-S System Under the Conditions of Operation of an Electric Smelting Furnace Treating Sulphide Concentrates (Cost Shared)

By

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ABSTRAIT

La phase d'equilibre du systeme Fe-Ni-Cu-S, ont ete examines. La limite de saturation de metaux fut identifier en determinant par une phase d'alliage metallique, le liens qui joignent les mattes de nickel-cuivre-fer, avec des temperatures de 1473 K a 1673 K.

La teneur de soufre diminue, dans une matte a saturation metallique, tout en augmentant le rapport de nickel/cuivre au fer. Ce rapport diminue lorsque la temperature augmente mais, n'est pas aussi sensible a la substitution du nickel pour le cuivre et vice versa pour la gamme de composition de matte examiner.

ABSTRACT

The phase equilibria in the Fe-Ni-Cu-S system were investigated. The metal saturation boundary was identified by determining the tie lines which join the nickel-copper-iron mattes with the metallic alloy phase at temperatures between 1473 to 1673 K.

The sulphur content of the matte at metal saturation decreased with increasing ratio of nickel plus copper to iron, and decreased as the temperature increased, but was insensitive to the substitution of nickel for copper and vice versa for the matte composition range examined.

INTRODUCTION

When nickel-copper concentrates are subjected to a roast operation, iron sulphide and a small amount of nickel sulphides are oxidized. In order to recover the oxidized nickel, a reductive smelting operation is performed. During this procedure, and in the presence of sulphur deficiency, a metallic phase can result.

The purpose of this study is to identify the metal saturation boundary as a function of temperature and composition.

EXPERIMENTAL

The general procedure adopted for this study involved the equilibration of Fe-Ni alloys with Fe-Ni-Cu-S mattes in either quartz or alumina crucibles at the required temperature for a period of time under an argon atmosphere. Samples of the sulphide phase were taken by suction into a quartz tube which was then quenched. The metal phase was sampled by cooling the crucible that contained the original melt. Microscopic examinations were carried out to insure that the matte sample was free of primary metallics prior to chemical analysis. The primary metal phase in the crucible was analyzed by use of the scanning electron microscope (SEM).

A. Sample Preparation

The metals used for this study were electrolytic grade nickel, electrolytic grade copper, reagent grade iron and vacuum sublimated sulphur. Prior to use, the metals were all hydrogen reduced at 773 K to eliminate oxygen.

The iron-nickel alloys were prepared by melting the required iron and nickel in an induction furnace under a nitrogen atmosphere. The composition of these alloys is shown in Table 1.

Copper sulphide, nickel sulphide and iron sulphide were prepared by vacuum sealing the required amounts of respective metal and sulphur in quartz ampoules. The sealed ampoules were heated to 723 K for 72 h to allow the sulphur gas to react with the metal phase. Once the sulphur had reacted, the ampoules were heated to approximately 1473 K to melt and homogenize the sulphide, after which the samples were cooled.

The metal saturation line for the Fe-Ni-S system has been determined over the temperature 1473-1673 K by Lenz et.al. [1]. Using this work as the basis, the metal saturation boundary was evaluated with the addition of copper sulphide to the matte phase. Metal in the range 9 to 15 g, depending on the temperature and matte grade, were equilibrated with matte in the range 11 to 5 g.

B. Apparatus

The apparatus used for this study is shown in Fig. 1. It consists of a molybdenum furnace with a mullite reaction tube into which the sample containing the matte and alloy phase was placed. Argon was passed over a copper getter furnace (723 K) to remove oxygen, then passed into the reaction tube.

To obtain samples of matte, a 5 mm diameter quartz tube was used.

C. Equilibration Time

The time required to equilibrate the matte and metal phase was determined by keeping samples of identical chemical composition during 24, 48, 72 and 96 h at 1473 K. These samples were rapidly cooled, microscopically observed and analyzed for nickel and sulphur in the sulphide and metal phase. After 48 h, the upper sulphide and bottom metallic portion of the sample did not show change in composition, as shown in Fig. 2. From these series of experiments, 48 h was selected as the "equilibrium time".

At 1673 the equilibrium time was estimated as 32 h.

D. Chemical Analysis

The matte samples were examined optically, to insure that it was free of the primary metallic phase. The samples which were free of primary metallics were analyzed chemically by Falconbridge Ltd. The metallic samples were analyzed by SEM using five iron-nickel standards. A typical trace showing the Fe, Ni, Cu and S content every 3 μm along a line joining the centre of two metallic grains is illustrated in Fig. 3.

E. Experimental Procedure

The experimental procedure involved the following steps:

1. keeping the sample at the bottom of the furnace for 2 h to flush out any air

introduced during the charging step,

2. slowly raising of the sample to the test temperature (45 min),

3. keeping the sample at the test temperature for about 1 h,

4. raising the temperature by 122 K to dissolve, during 30 min, the metal phase

5. decreasing the temperature to the test temperature,

6. keeping the sample at the test temperature for about 46.5 h,

7. sampling of matte, and

8. slowly cooling the remaining sample to avoid breaking of the sample holder tube.

RESULTS AND DISCUSSIONS

The chemical analysis for the equilibrated metal-sulphide phases (represented by the letters M and S, respectively) are given in Table 2 for the tests at 1473 K, in Table 3 for 1573 K and in Table 4 for 1673 K.

The results are also plotted on a ternary diagram where the corners represent Fe, Ni+Cu and S. The results for 1473, 1573 and 1673 K are shown in Figures 4, 5 and 6 respectively. The tie lines are indicated by a join between the two conjugate solutions. For comparison, the data reported by Lenz et.al. [1] for the Fe-Ni-S system, denoted by dashed line and by Falconbridge [2] for the Fe-Ni-Cu-S system, denoted by full line, are shown.

For all the temperatures investigated Lenz et.al.'s results show lower sulphur contents, specially below 50% Ni+Cu, than those found in the present study. However, those reported by Falconbridge are significantly higher than those from this study, the difference being greater at higher temperatures.

In Figure 7, the Ni+Cu mass percent is plotted against mass per cent sulphur in the matte for the three temperatures investigated. The line represents the two phase equilibria between matte and the metallic phase. To the right of the line the matte phase is stable, while to the left of the line there is a two phase region of alloy plus matte.

The higher the Ni+Cu, the less sulphur is required to stabilize the matte phase. Once the equilibrium liquidus line is reached a further decrease in sulphur content results in the precipitation of a metallic iron-nickel-copper alloy. The three temperatures considered shown the same tendency in respect to this effect, i.e. a continuous increase in sulphur with decreasing Ni+Cu content in matte.

Evaluation of commercial mattes at 1573 K [3], represented by triangles in Figure 7, agree quite well with the present results. The location of the Ni+Cu and S content of these samples lay on the right side of the sulphide-metal equilibrium line and therefore they should correspond to a homogeneous sulphide phase, which in fact occurred.

Based on the data of Figure 7, the effect of temperature upon the dissolution of sulphur, for different Ni+Cu contents in matte, is shown in Figure 8. Similar curves to the ones shown can be worked out for any desired Ni+Cu content in matte at the temperatures investigated.

Given a specific Ni+Cu content in matte the lower the equilibrium temperature the higher the sulphur content in matte. For example for Ni+Cu = 50% at 1573 K the matte phase dissolves approximately 9% S, while decreasing the temperature to 1473 K results in an increase to 16.5% S.

At the lower matte grades, i.e. low Ni+Cu content, the matte consists mainly of iron sulphide therefore, the limiting sulphur content corresponds to that of the Fe-S system at the temperature considered. For example, the line representing the data at 1673 K will intersect the sulphur axis at 7%, while that at 1473 K does at 27% S.

The tendency observed in these curves is a decrease in sulphur with increasing temperature and with increasing matte grade. At 1473 K significant changes in sulphur content with matte grade occur. However, as the equilibration temperature increases the change in sulphur is less significant, i.e. at 1673 K.

The present results, Figure 7, clearly indicate that the input Ni to Cu ratio does not significantly affect the equilibrium distribution of Ni and Cu in the conjugate solution. It would appear that the replacement of Ni for Cu in the matte phase is additive. The additivity is particularly noticeable at the higher temperature. Thus, the more important compositional parameter is the mass percent of Ni+Cu.

CONCLUSIONS

The metal saturation line in the Fe-Ni-Cu-S system has been determined at temperatures of 1473 K, 1573 K and 1673 K. The input nickel to copper ratio in the matte phase does not significantly affect the equilibrium distribution of Ni and Cu in the conjugate phase.

Ni and Cu are similar in atomic size and consequently form a complete solid solution. The present work supports the validity of the assumption that the total concentration of nickel plus copper is an important compositional parameter governing the metal saturation boundary for nickel-copper-iron mattes in the compositional range examined.

REFERENCES

1. J.G. Lenz, B.R. Conard, R. Sridhar and J.S. Warner: Met. Trans. 9B (1978), 459-462

2. Hatch Associates Ltd.: Internal Report - Falconbridge 1988

3. C.M. Acuna and J.M. Toguri: Metal Saturation Studies of Commercial Matte Samples from Falconbridge, Report- Falconbridge March 1991

ANNEX OF TABLES

Table 1: Composition of Prepared Samples

	Mass percent, %			
	Fe	Ni	Cu	S
A) Sulphides:				
Iron sulphide	70.96	-----	-----	29.04
Nickel sulphide	-----	87.34	-----	12.66
Copper sulphide	-----	-----	79.73	20.27
B) Alloys:				
Iron-10% Ni	87.04	12.96	-----	-----
Iron-30% Ni	67.72	32.28	-----	-----
Iron-50% Ni	47.61	52.39	-----	-----
Iron-70% Ni	28.31	71.69	-----	-----
Iron-90% Ni	10.52	89.48	-----	-----

Table 2: Results of chemical analysis for samples with different nickel to copper ratios equilibrated at 1473 K.

Sample Number	Chemical Composition (Mass percent, %) As reported Ni	Cu	Fe	S	Normalized Ni	Cu	Fe	S
Ni : Cu = 1 : 3								
1S	4.05	5.06	61.9	26.0	4.17	5.22	63.81	26.80
1M					6.60	1.22	92.18	-----
2S	11.8	13.0	49.8	23.1	12.08	13.31	50.97	23.64
2M					21.69	3.94	74.37	-----
3S	24.1	19.4	34.0	19.6	24.82	19.98	35.02	20.18
3M					39.55	8.76	51.69	-----
4S	41.4	20.6	22.7	11.5	43.04	21.41	23.60	11.95
4M					54.54	12.86	32.60	-----
5S	70.0	16.3	6.3	9.6	68.49	15.95	6.17	9.39
5M					78.17	11.92	9.91	-----
Ni : Cu = 1 : 1								
1S	5.3	3.3	64.6	25.4	5.38	3.35	65.51	25.76
1M					8.33	0.84	90.83	-----
2S	15.5	8.75	51.1	22.5	15.84	8.94	52.22	23.00
2M					25.05	3.10	71.85	-----
3S	34.2	10.3	35.1	16.8	35.48	10.68	36.41	17.43
3M					47.40	5.34	47.26	-----
4S	44.6	16.7	22.2	12.0	46.70	17.48	23.25	12.57
4M					57.98	10.34	31.78	-----
5S	61.6	18.4	7.5	9.0	63.83	19.07	7.77	9.33
5M					74.64	13.53	11.83	-----
Ni : Cu = 3 : 1								
1S	6.7	1.7	64.6	24.5	6.87	1.74	66.26	25.13
1M					10.15	0.49	89.36	-----
2S	19.2	4.5	53.4	21.9	19.39	4.55	53.94	22.12
2M					28.67	1.57	69.76	-----
3S	37.9	5.14	36.1	16.9	39.46	5.35	37.59	17.60
3M					49.64	2.79	47.57	-----
4S	51.2	9.4	22.6	12.8	53.33	9.80	23.54	13.33
4M					63.95	5.70	30.35	-----
5S	66.6	10.7	7.6	10.1	70.11	11.26	8.00	10.63
5M					80.03	7.98	11.99	-----

Table 3: Results of chemical analysis for samples with different nickel to copper ratios equilibrated at 1573 K.

Sample Number	Chemical Composition (Mass percent, %) As reported Ni	Cu	Fe	S	Normalized Ni	Cu	Fe	S
Ni : Cu = 1 : 3								
1S	6.0	4.6	66.0	23.2	6.01	4.61	66.13	23.25
1M					7.93	0.99	91.08	-----
2S	19.0	9.0	55.0	17.1	18.98	8.99	54.95	17.08
2M					24.07	3.64	72.29	-----
3S	40.5	8.8	43.0	8.8	40.07	8.70	42.53	8.70
3M					44.51	5.11	50.38	-----
4S	56.8	12.5	26.8	6.4	55.41	12.20	26.15	6.24
4M					56.73	8.10	35.17	-----
5S	74.5	14.5	8.5	6.0	71.98	14.01	8.21	5.80
5M					78.15	11.16	10.69	-----
Ni : Cu = 1 : 1								
1S	7.1	2.85	66.8	22.8	7.14	2.86	67.10	22.90
1M					8.87	0.71	90.42	-----
2S	21.5	6.3	55.5	16.6	21.52	6.30	55.56	16.62
2M					25.57	2.72	71.71	-----
3S	42.8	6.3	42.0	9.05	42.74	6.28	41.94	9.04
3M					46.37	3.94	49.69	-----
4S	58.0	9.3	25.5	7.2	58.00	9.30	25.50	7.20
4M					62.77	6.04	31.19	-----
5S	73.5	12.5	8.3	5.7	73.50	12.50	8.30	5.70
5M					80.03	9.05	10.92	-----
Ni : Cu = 3 : 1								
1S	8.0	0.60	65.0	22.6	8.32	0.62	65.57	23.49
1M					10.49	0.54	88.97	-----
2S	24.8	3.05	55.5	15.6	25.06	3.08	56.09	15.77
2M					28.47	1.36	70.17	-----
3S	45.3	3.53	40.8	9.34	45.77	3.57	41.22	9.44
3M					49.16	2.06	48.78	-----
4S	62.8	5.55	24.8	7.5	62.39	5.50	24.64	7.45
4M					66.41	3.77	29.82	-----
5S	77.5	7.0	7.8	6.8	78.20	7.06	7.88	6.86
5M					84.57	4.96	10.47	-----

Table 4: Results of chemical analysis for samples with different nickel to copper ratios equilibrated at 1673 K.

Sample Number	Chemical Composition (Mass percent, %) As reported Ni	Cu	Fe	S	Normalized Ni	Cu	Fe	S
Ni : Cu = 1 : 3								
1S	12.0	1.19	81.6	4.75	12.06	1.19	81.98	4.77
1M					10.72	0.72	88.56	-----
2S	30.2	1.93	64.5	2.55	30.45	1.95	65.03	2.57
2M					28.73	1.29	69.98	-----
3S	49.5	1.60	44.8	1.68	50.73	1.64	45.91	1.72
3M					51.08	1.06	47.86	-----
4S	66.5	2.51	27.2	1.22	68.25	2.58	27.92	1.25
4M					69.60	1.70	28.70	-----
5S	84.5	3.15	9.0	1.39	86.19	3.21	9.18	1.42
5M					88.86	2.20	8.94	-----
Ni : Cu = 1 : 1								
1S	12.0	0.78	81.6	4.77	12.10	0.79	82.30	4.81
1M					11.35	0.62	88.03	-----
2S	29.8	1.26	66.2	2.65	29.83	1.26	66.26	2.65
2M					28.75	0.87	70.38	-----
3S	50.0	1.16	44.8	1.71	51.19	1.19	45.87	1.75
3M					51.15	0.77	48.08	-----
4S	68.5	1.27	27.0	1.07	70.01	1.30	27.60	1.09
4M					70.78	0.92	28.30	-----
5S	85.5	2.20	8.8	2.03	86.78	2.23	8.93	2.06
5M					89.28	1.60	9.12	-----
Ni : Cu = 3 : 1								
1S	12.9	0.42	82.1	4.15	12.96	0.42	82.45	4.17
1M					11.36	0.48	88.16	-----
2S	30.0	0.68	66.4	2.75	30.05	0.68	66.51	2.76
2M					29.49	0.64	69.87	-----
3S	50.5	0.61	44.8	1.40	51.90	0.62	46.04	1.44
3M					51.00	0.64	48.36	-----
4S	68.5	1.11	27.0	1.11	70.09	1.14	27.63	1.14
4M					71.07	0.71	28.22	-----
5S	86.5	1.24	9.0	1.49	88.06	1.26	9.16	1.52
5M					89.78	1.05	9.17	-----

ANNEX OF FIGURES

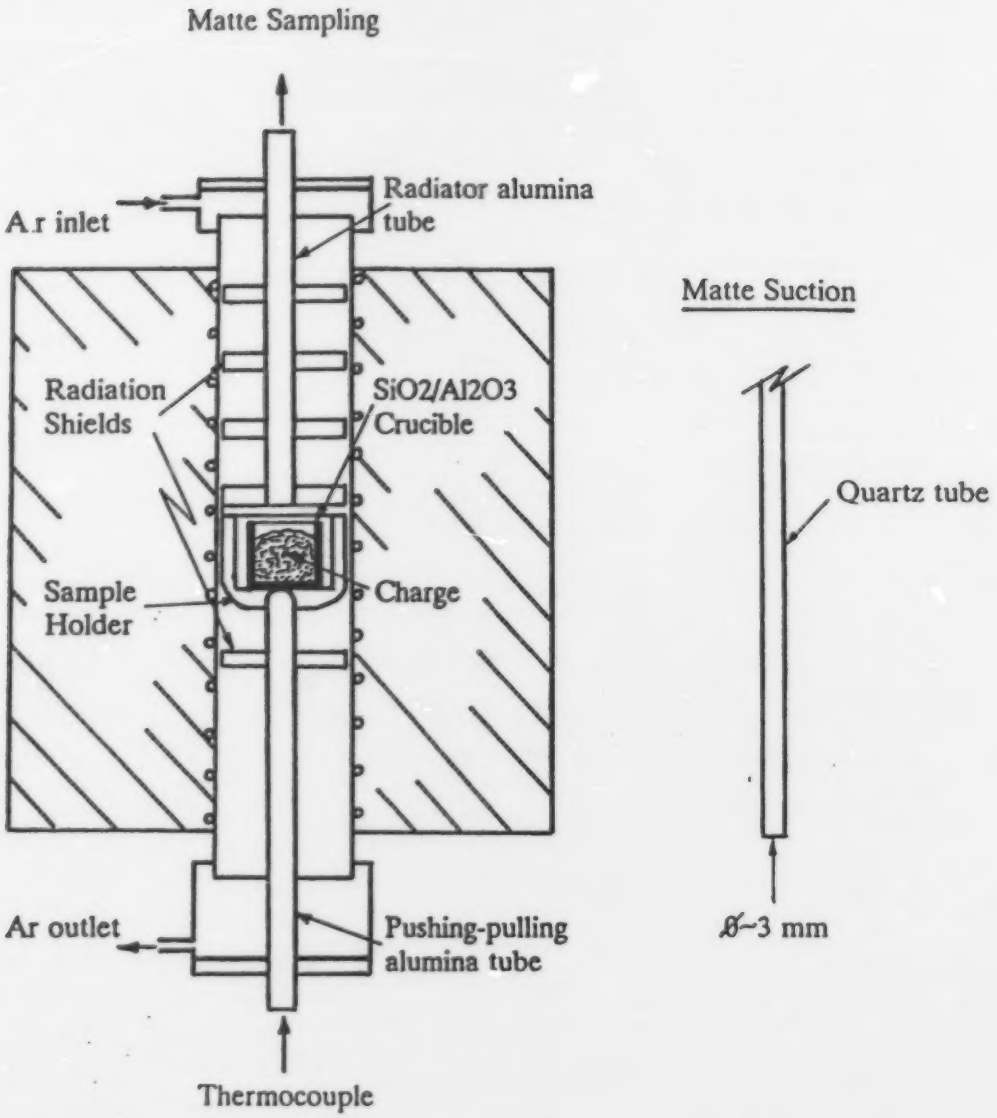

Figure 1: Schematic representation of the furnace set up.

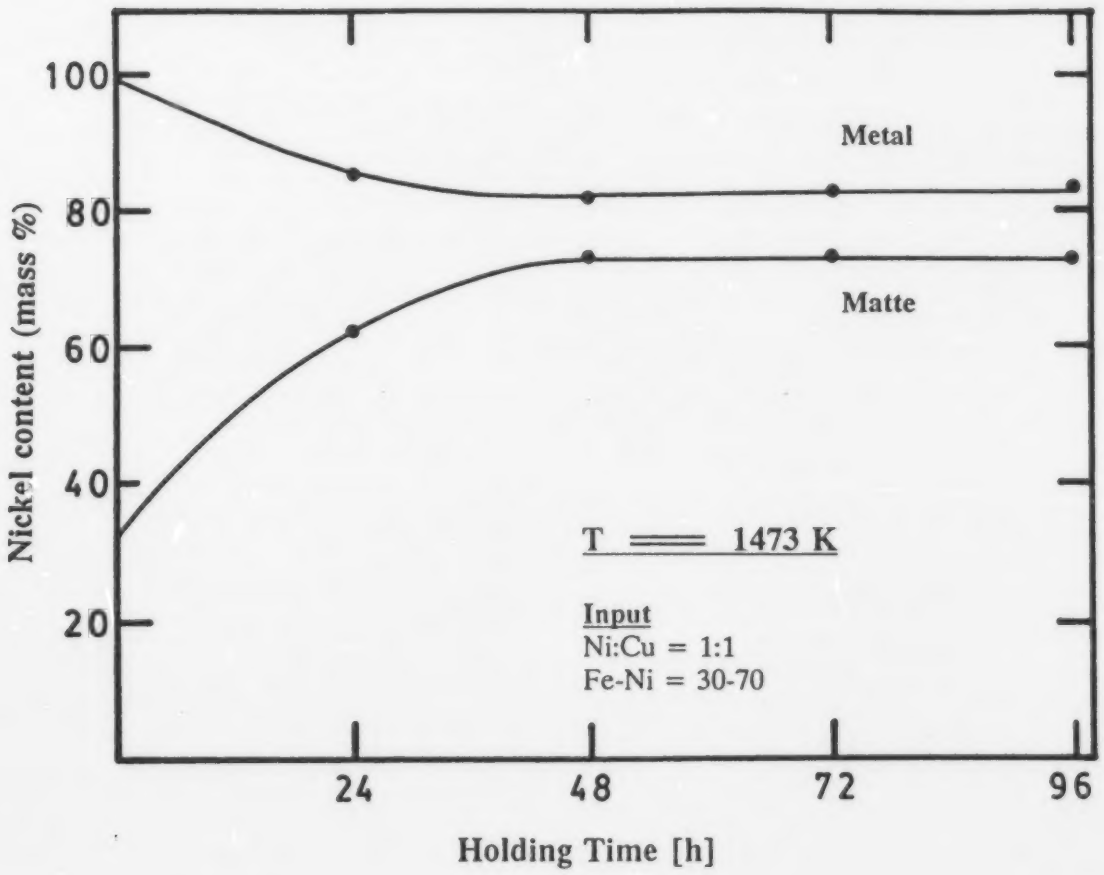

Figure 2: Determination of the "equilibrium time". It corresponds to the time where the plateau for nickel content in matte and metal is reached

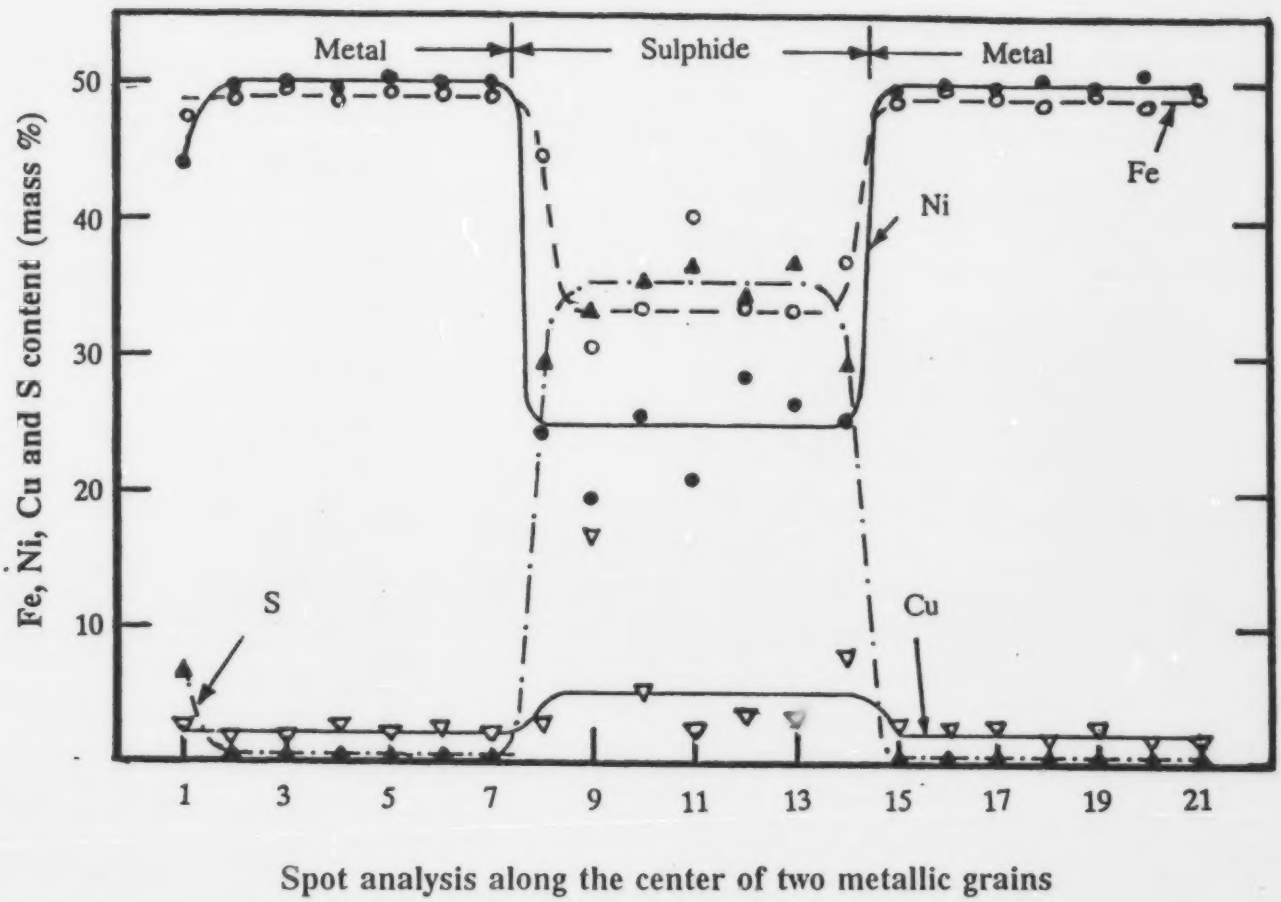

Figure 3: Gradient concentration along the line joining the centre of two metallic grains.

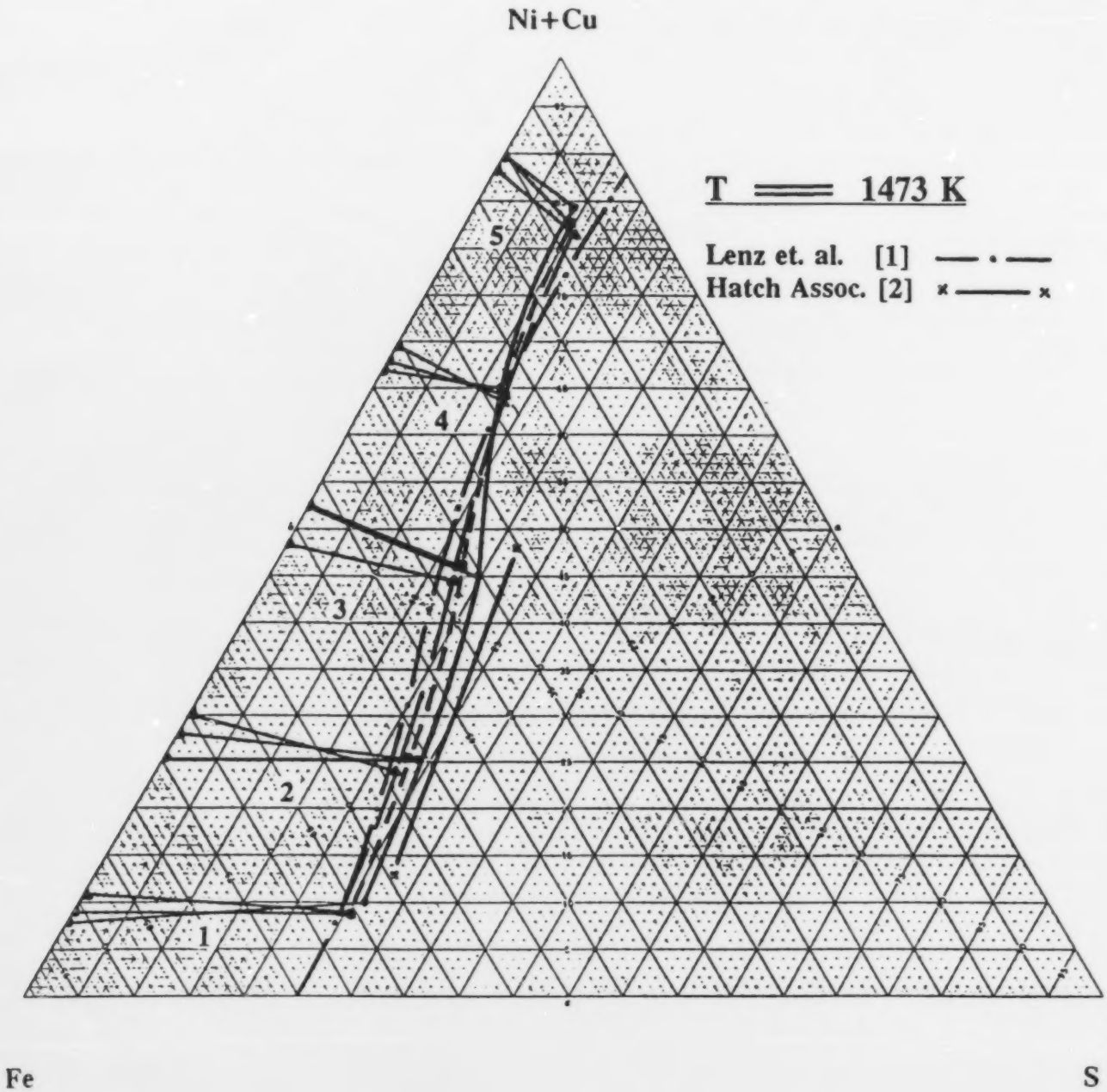

Figure 4: Representation of experimental results on a Fe-Ni+Cu-S pseudoternary system at 1473 K.

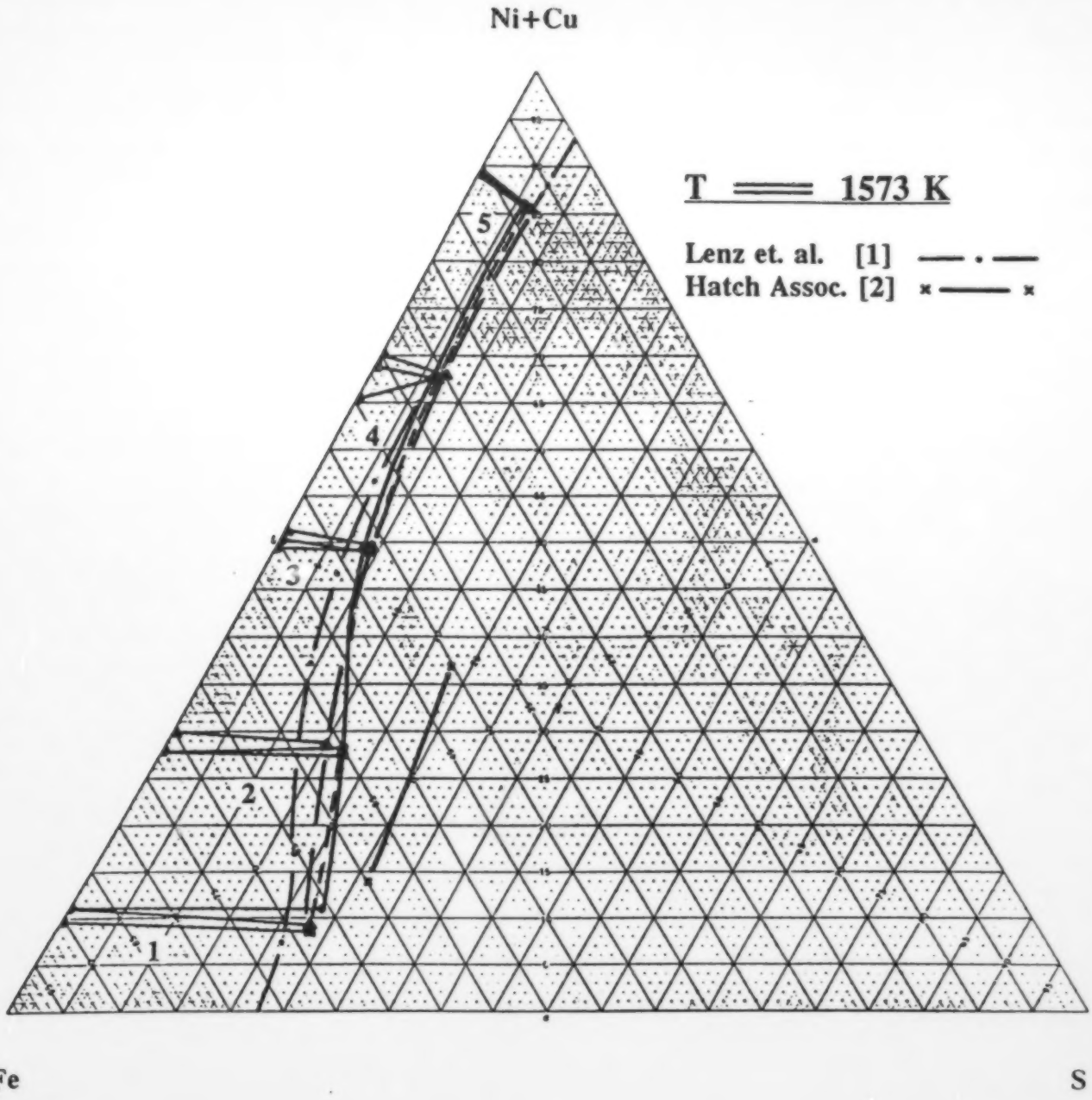

Figure 5: Representation of experimental results on a Fe-Ni+Cu-S pseudoternary system at 1573 K.

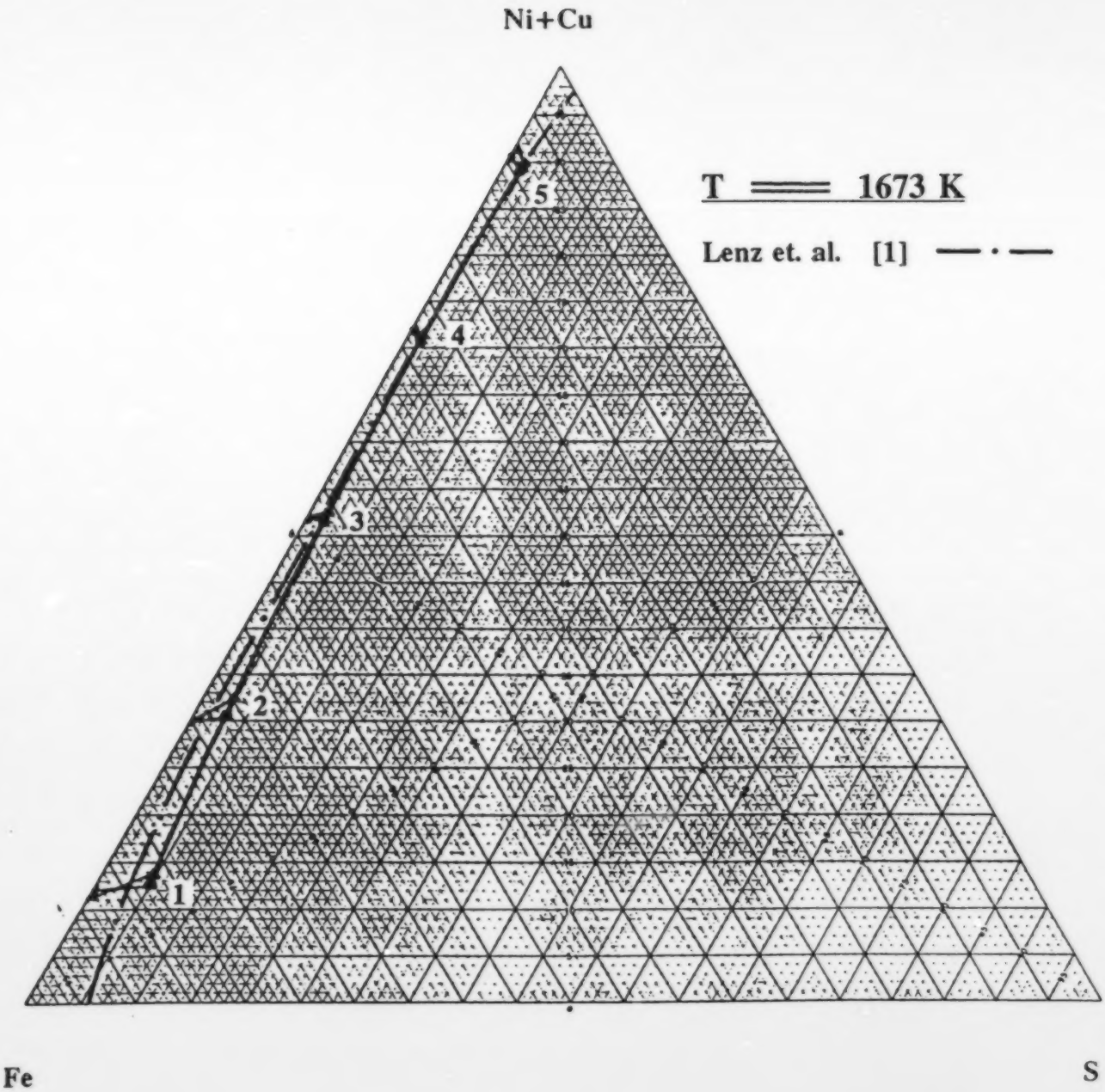

Figure 6: Representation of experimental results on a Fe-Ni+Cu-S pseudoternary system at 1673 K.

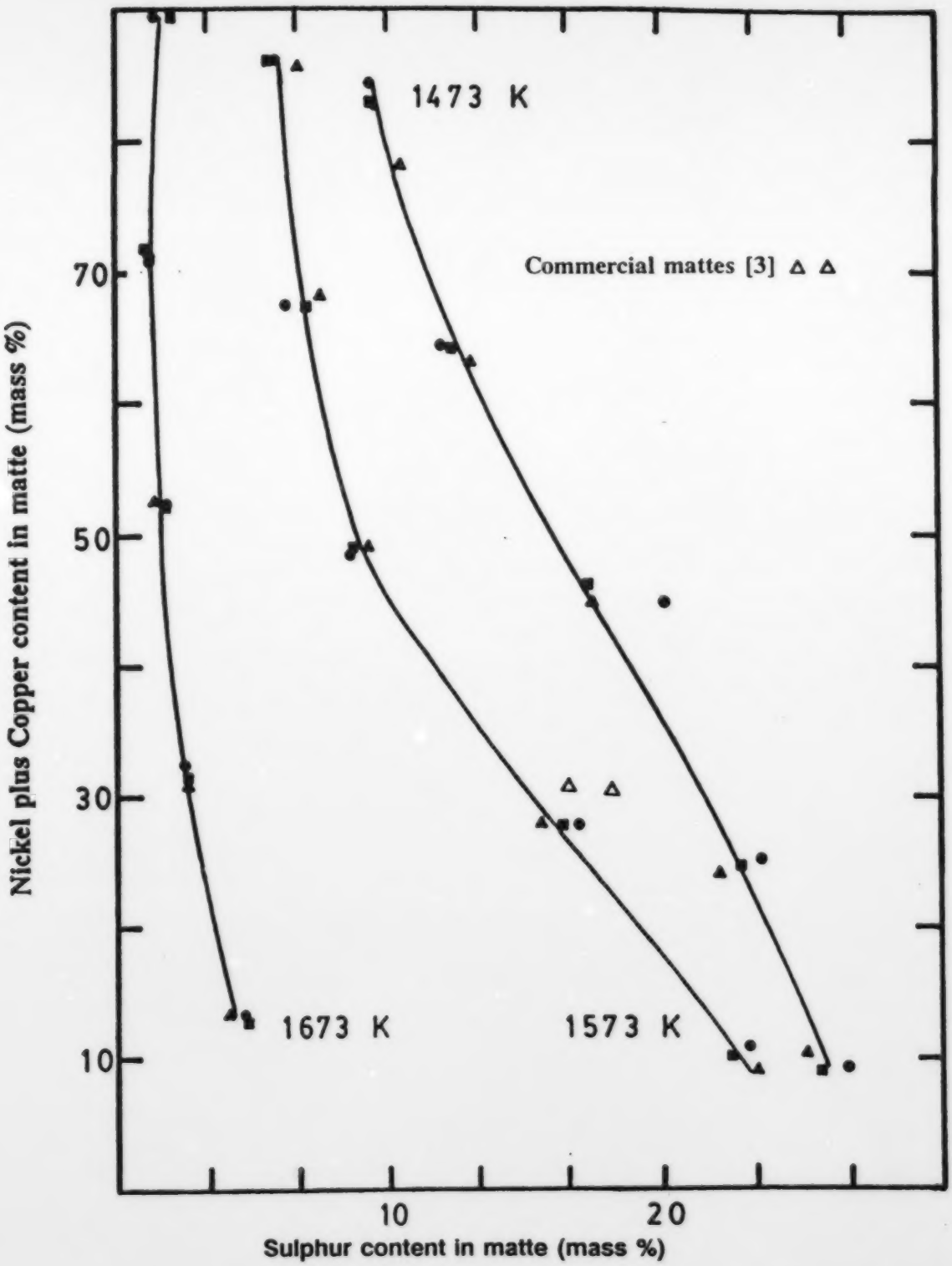

Figure 7: Effect of nickel plus copper on sulphur content in matte at different Ni:Cu ratios and temperatures

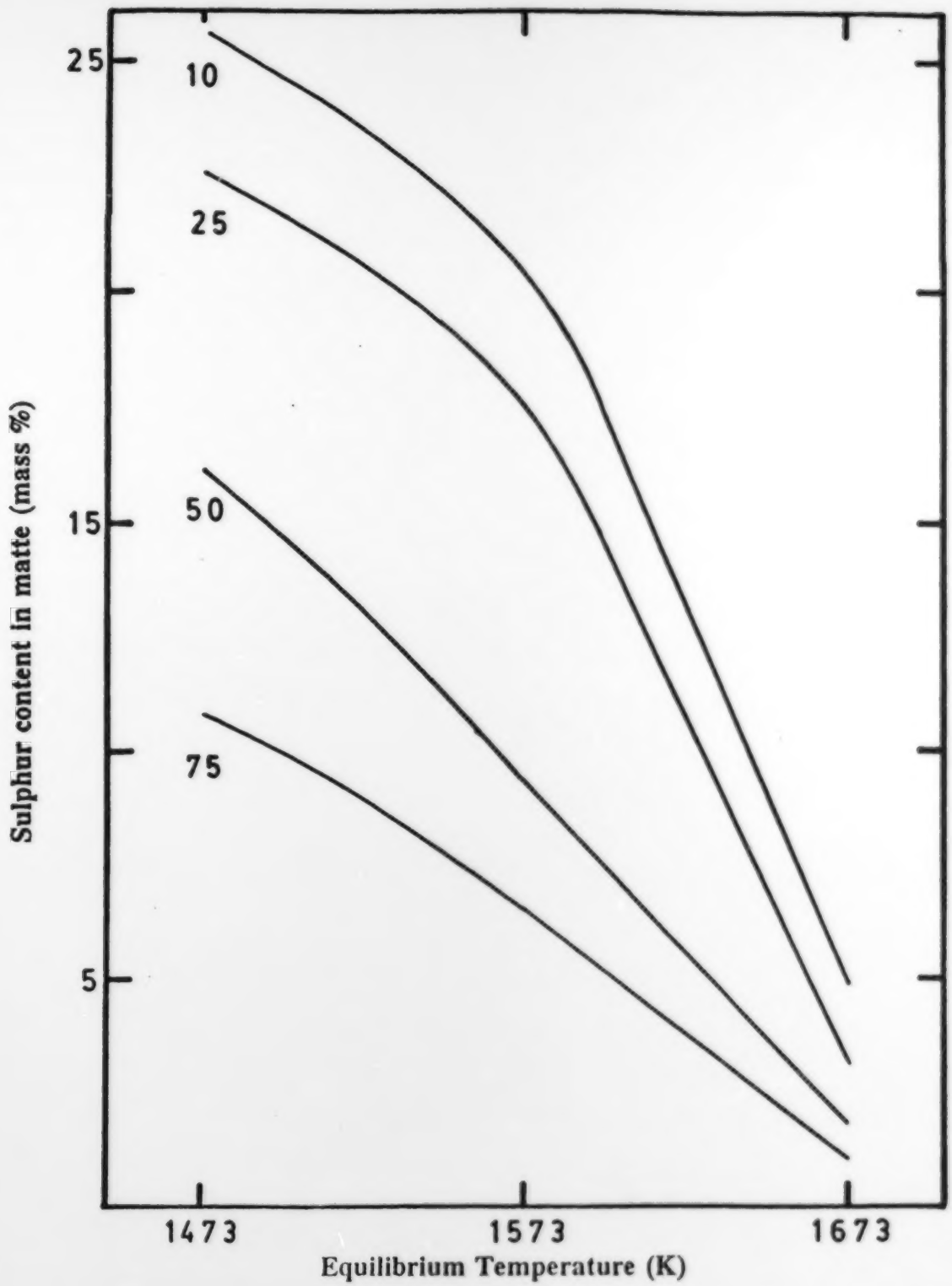

Figure 8: Relationship between the matte grade (Ni+Cu, denoted by the numbers below the curves) and its sulphur content at different temperatures.